



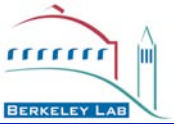
# Quantifying California's Greenhouse Emissions with Atmospheric Inverse Approaches: The CALGEM Project

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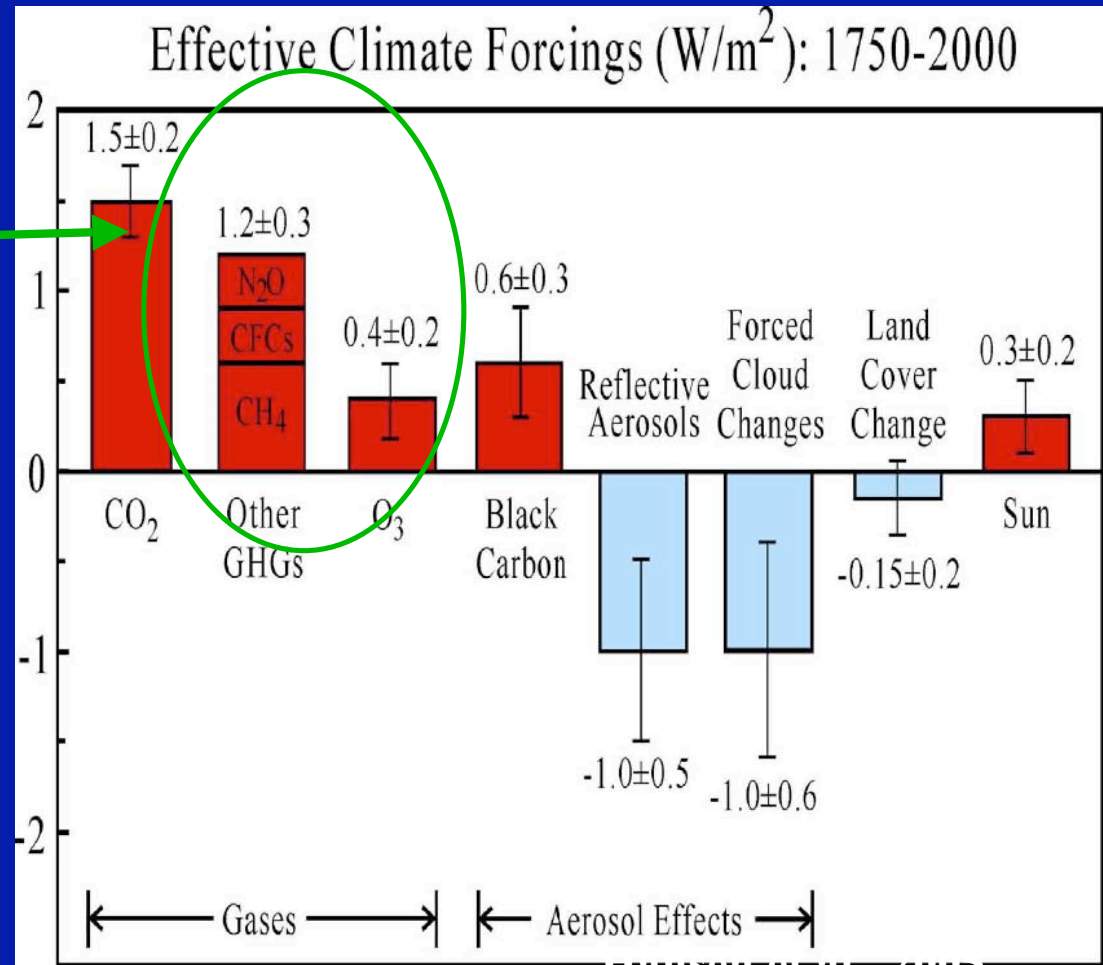


# Outline

- Overview of GHG trends
  - Focus on California emissions
- CALGEM Measurements
- Two Inverse Approaches
  - “Gas ratio” or “unknown:known”
  - “Formal Inverse”: Optimize *a priori* emissions to match measurements using meteorological and Bayesian statistical models
- Summary
- Further work

# Climate Forcing Pre-Industrial - Present

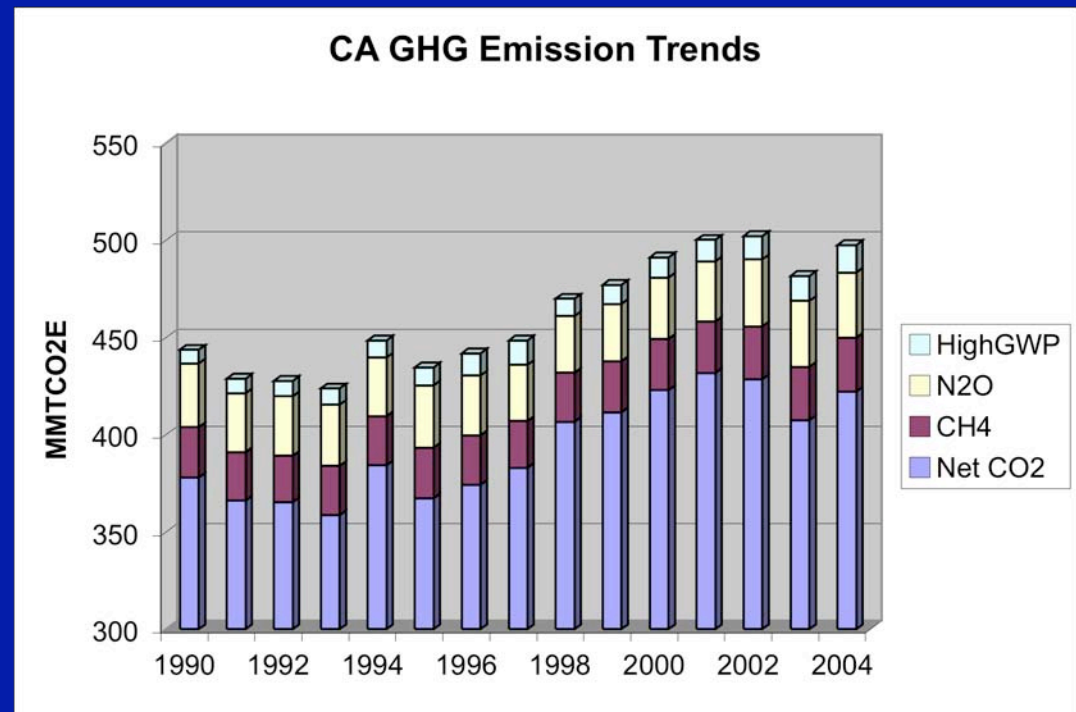
- Total non-CO<sub>2</sub> GHG forcing ~ equivalent to CO<sub>2</sub> forcing globally
- Non-CO<sub>2</sub> gases much stronger absorbers than CO<sub>2</sub> by mass
  - CH<sub>4</sub> ( ~ 20 x CO<sub>2</sub>)
  - N<sub>2</sub>O ( ~ 300 x CO<sub>2</sub>)
  - High GWP (e.g., CFCs, HFCs, SF<sub>6</sub>) ( ~ 10<sup>3</sup> - 10<sup>4</sup> x CO<sub>2</sub>)
  - Tropospheric ozone



Hansen et al., 2005

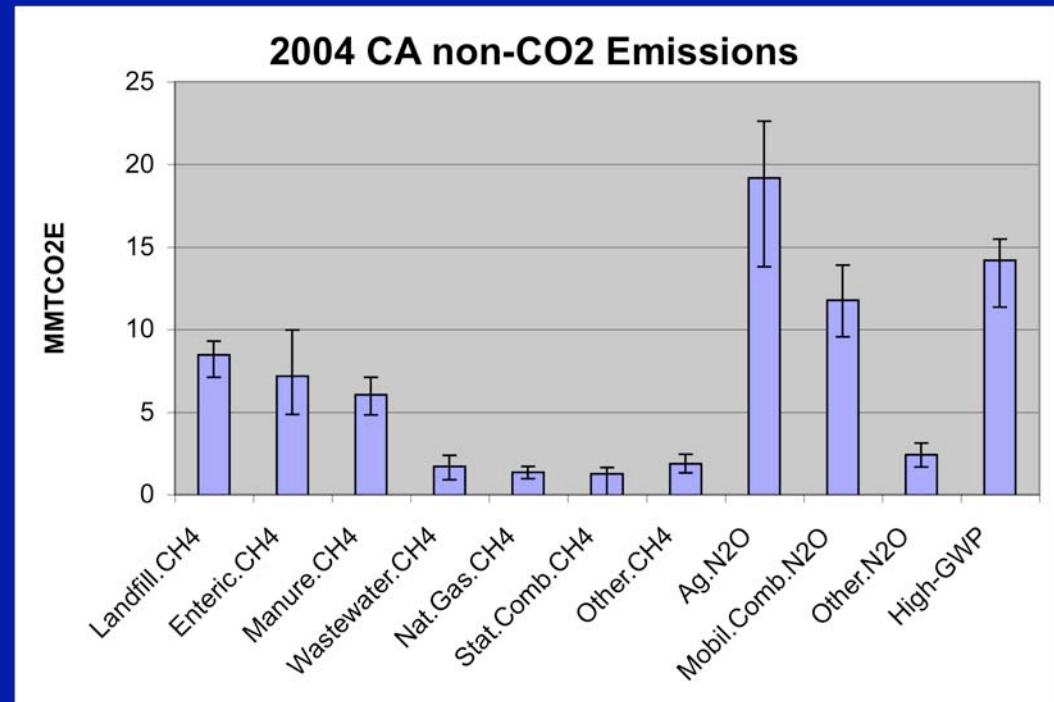
# California GHG Emission Trends

- CO<sub>2</sub> dominates GHG emissions
  - Controls must start with CO<sub>2</sub>
- Non-CO<sub>2</sub> gases more uncertain
  - Opportunities for control exist in this sector
  - Quantifying current emissions important



# California non-CO<sub>2</sub> GHG Emissions

- Non-CO<sub>2</sub> GHGs largely from biological sources
- Uncertainties are large
  - many sources not readily metered
  - Some gases not currently included (e.g. CFCs)
- Atmospheric approaches can provide independent constraints
- Evaluation of uncertainties is an essential challenge



CEC, 2006 ; USEPA, 2007



# CALGEM Measurement Sites

**Sutro Tower (232 m agl)**  
**Oceanic + urban**

**Walnut Grove (483 m agl)**  
**Valley + Bay Area**



# Instrumentation

- Both Sites: 12 Flask System

- Twice daily samples
- $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$
- high GWP gases
- $^{13}\text{CO}_2$ ,  $^{13}\text{CH}_4$ ,  $\text{CDH}$



- Walnut Grove:

- $\text{CH}_4/\text{CO}_2$  analyzer- 3min
- $\text{CO}_2/\text{CO}$  rack – 3 min
- $^{222}\text{Rn}$  monitor – 30 min
- $^{14}\text{CO}_2$  (w/ LLNL)

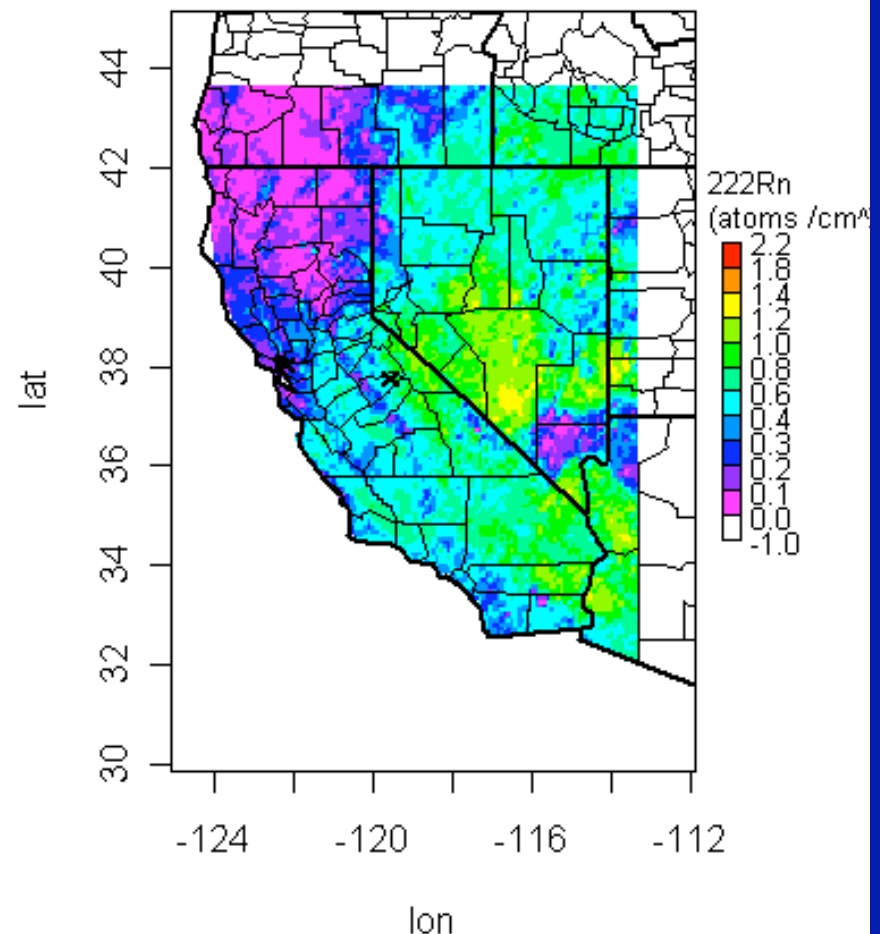




# Atmospheric Tracers

- $^{222}\text{Rn}$  Radon from soils
  - Short half life (3.8 day) gives atmospheric contact with terrestrial systems
  - Emission rate depends on  $^{238}\text{U}$  soil content, moisture
  - Need CA specific model calibration including soil moisture
- CO - combustion tracer
- Isotopes
  - $^{14}\text{CO}_2$  none in fossil fuel
  - $^{13}\text{CO}_2$  (Nat gas vs. gasoline)
  - $^{13}\text{CH}_4$ ,  $\text{CDH}_3$  (landfills, vs. nat. gas)

Relative  $^{222}\text{Rn}$  Radon Flux



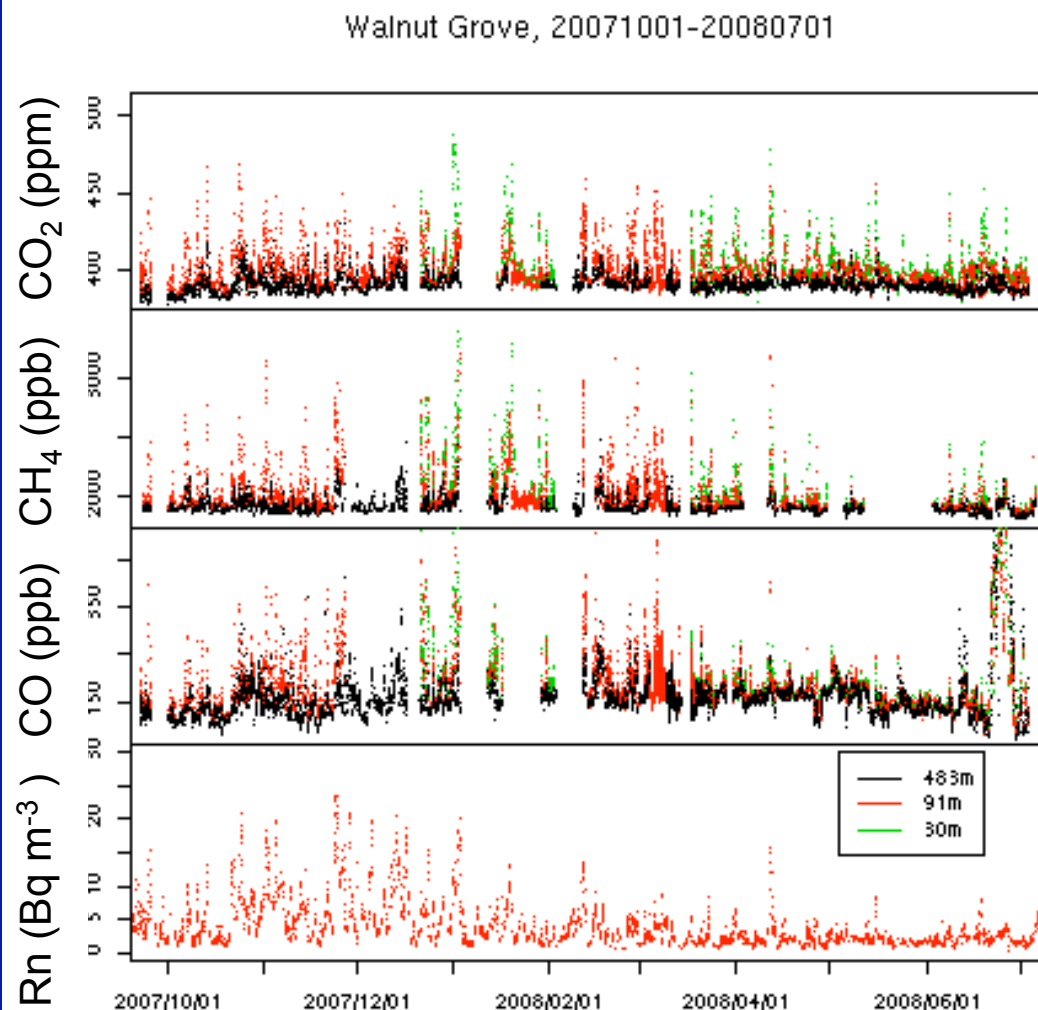
(Szegvary, 2006)



# In-situ Measurements at Walnut Grove

First 9 months reveal:

- Elevated mixing ratios at 30, 91m indicate strong regional-local emissions
- Strong correlation of diurnal variations in  $\text{CO}_2$ ,  $\text{CH}_4$  and  $^{222}\text{Rn}$  implicates variations in boundary layer
- Synoptic variations offer opportunity to extract emissions information
- 483 m mixing ratios generally near background levels at night (decoupled from surface)



# Gas-Ratio Approach (1)

## GHG emissions from $^{222}\text{Rn}$ Correlation

Mixing model for GHG flux:

$$\langle F_x \rangle = \langle F_{\text{Rn}} \rangle * dC_x/dC_{\text{Rn}}$$

(if  $\langle F_{\text{Rn}} \rangle = 0.3 \text{ atom cm}^{-2} \text{ s}^{-1}$ )

$$F_{\text{CO}_2} \sim 35 \text{ t CO}_2/\text{ha/yr}$$

$$F_{\text{CH}_4} \sim 200 \text{ kg CH}_4/\text{ha/yr}$$

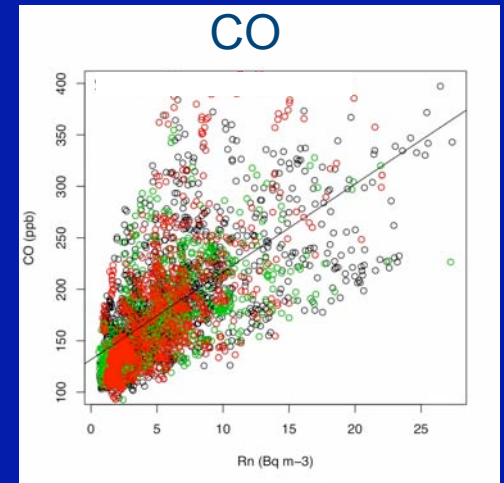
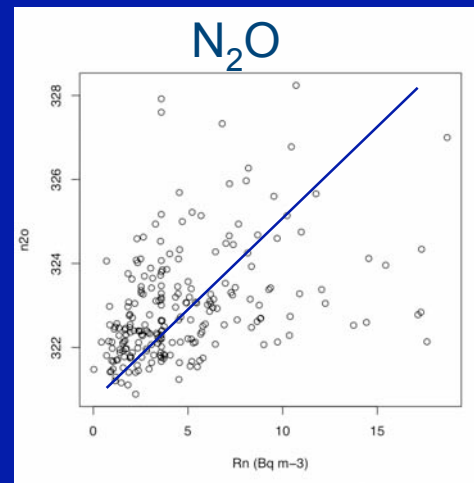
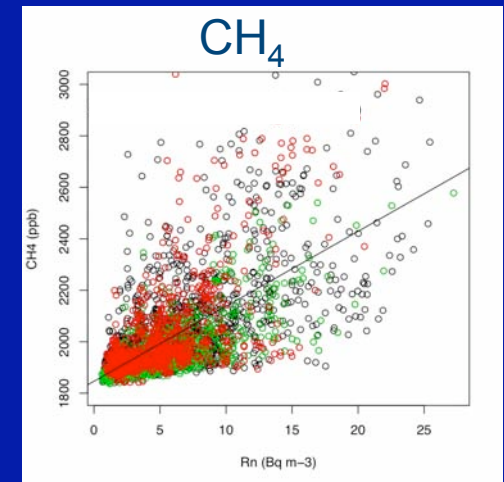
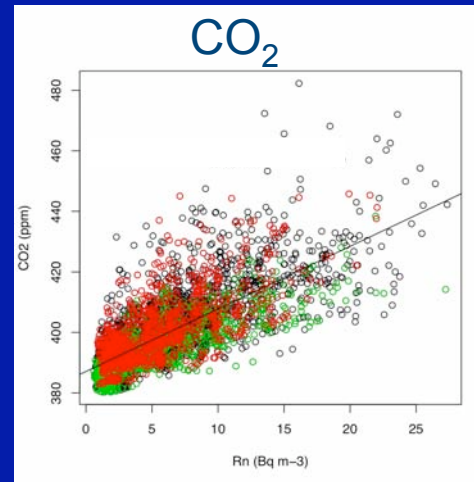
$$F_{\text{N}_2\text{O}} \sim 5 \text{ kg N}_2\text{O}/\text{ha/yr}$$

$$F_{\text{CO}} \sim 130 \text{ kg CO}/\text{ha/yr}$$

note: slopes all estimated to  $< 10\%$

Next steps:

- Check Rn emissions
  - Trends might be determined if Rn emissions remain constant (Messenger, 2008)
- Use CO as an alternate tracer



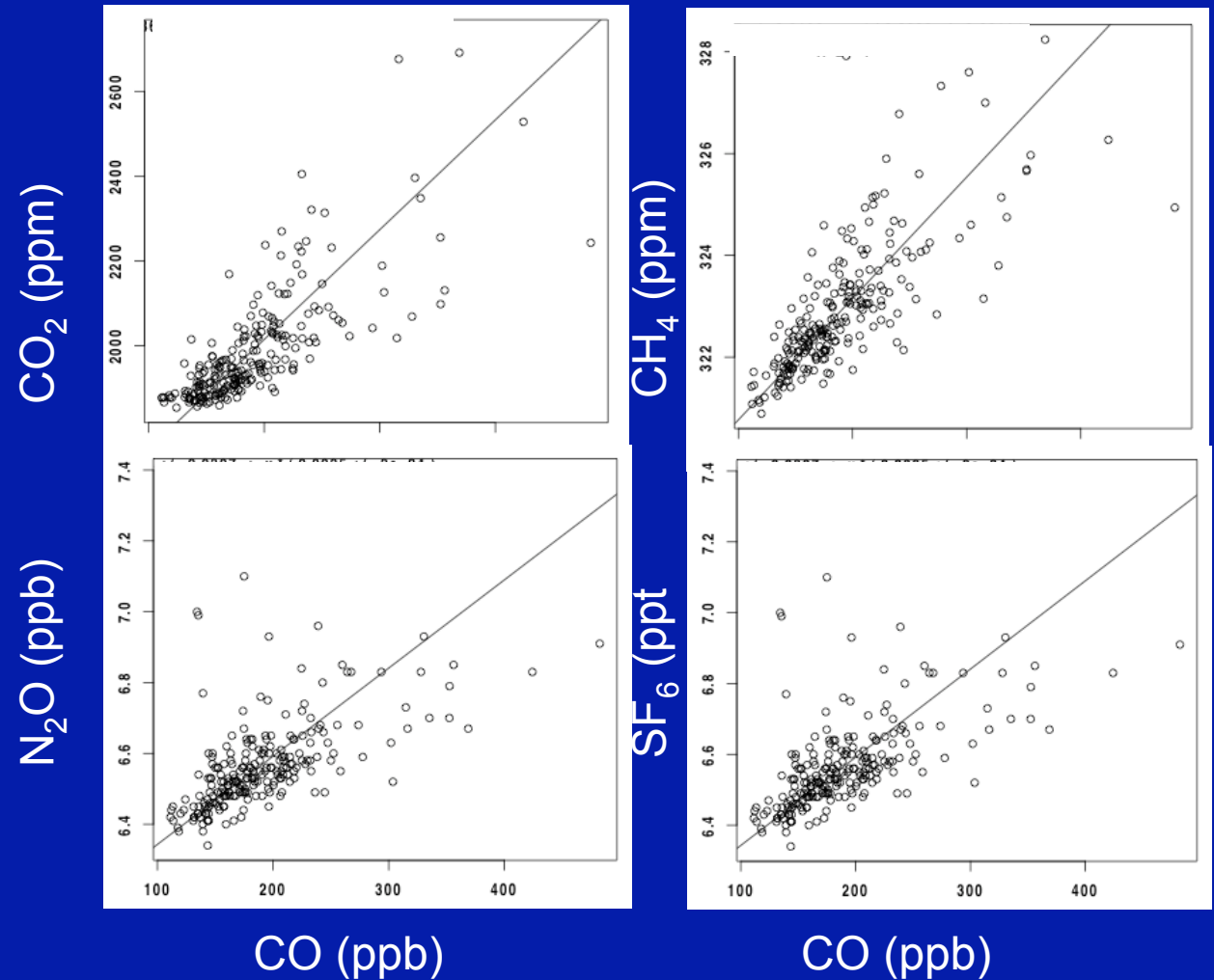
$\text{Rn}$  ( $\text{Bq m}^{-3}$ )

$\text{Rn}$  ( $\text{Bq m}^{-3}$ )

# Gas-Ratio Approach (2)

## GHG correlations with CO

- High correlations to CO yield accurate estimates of slope
- Need footprint weighted CO emissions for use in estimating GHG emissions



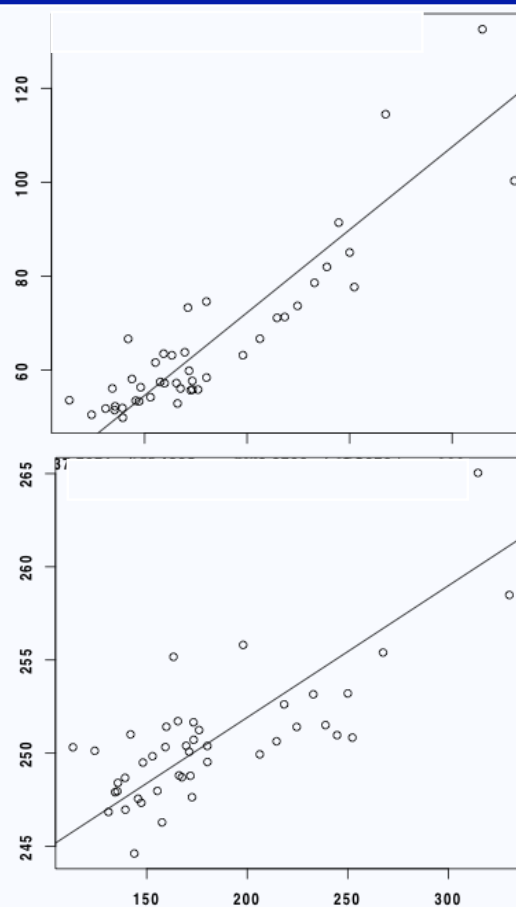
# Gas-Ratio Approach (2)

## High-GWP Gas Emissions

- Good Rn (and CO) correlations obtained for several important high-GWP gases
- Applying Rn mixing model yields estimated emissions for 14 high-GWPs in central CA
- If high-GWP gas emissions similar in other populated areas then emissions are  $\sim 14$   $\text{MtCO}_{2\text{equiv}} \text{ yr}^{-1}$
- Find CFC11 and CFC12 emissions are also  $\sim 10$   $\text{MtCO}_{2\text{equiv}} \text{ yr}^{-1}$ , similar to other high-GWP gases

HFC134A (ppt)

CFC11 (ppt)

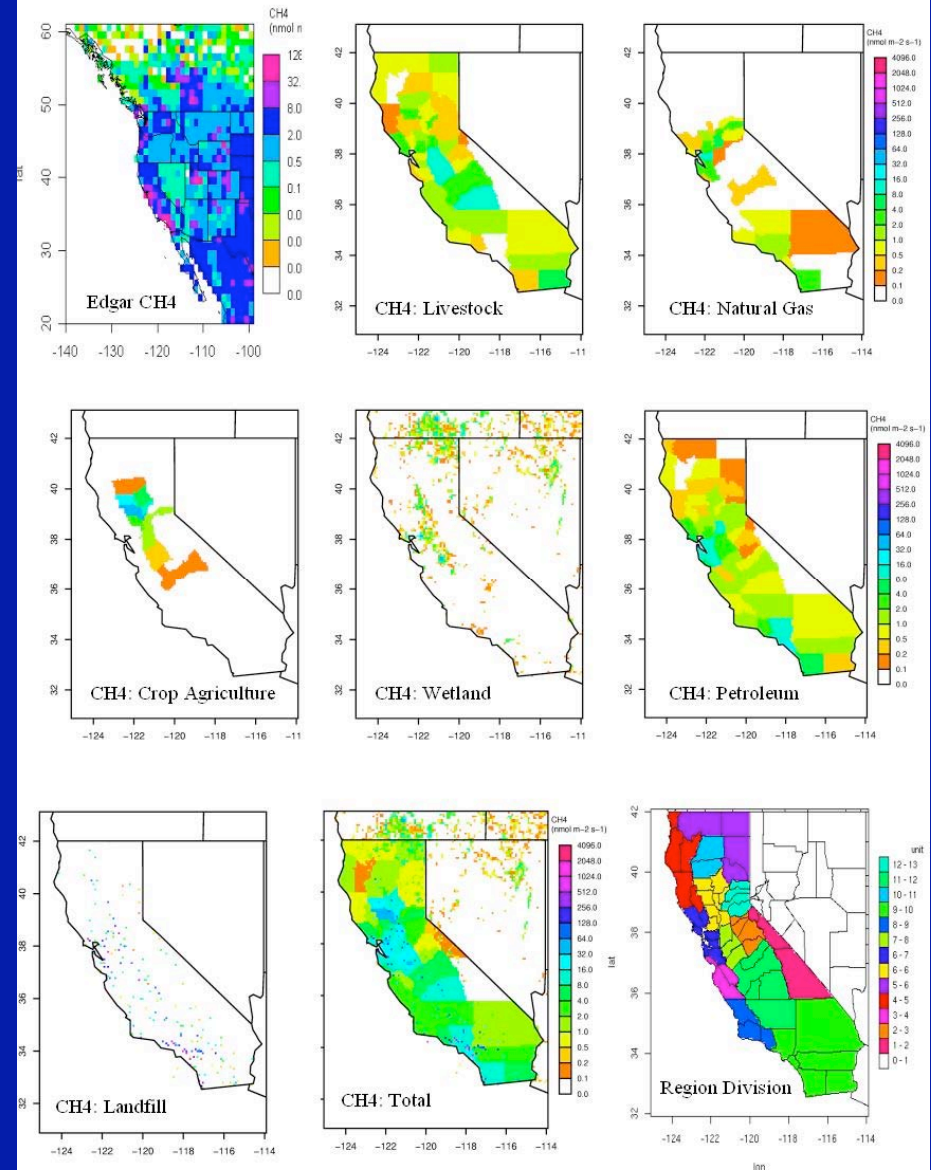


CO (ppb)



# Formal Inverse (1) *a priori* CH<sub>4</sub> Flux Maps

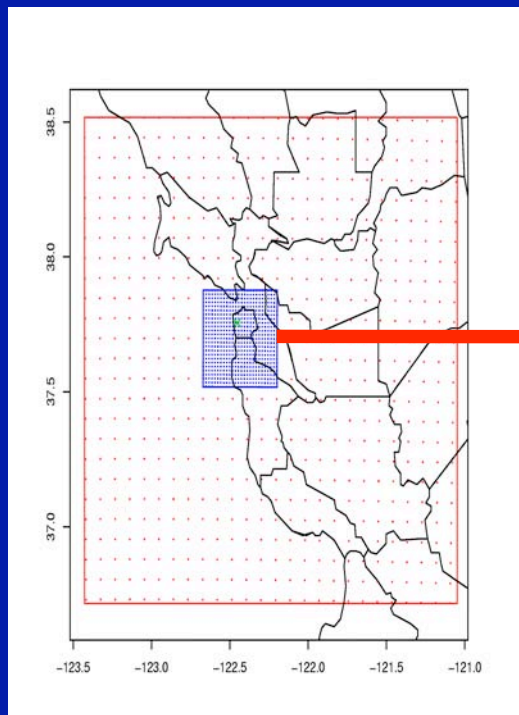
- EDGAR3.2 (1x1degree)
- Landfill (point sources)
  - Landfill specific loading with substrate dependent residence time (EPA)
- Animal Ag. (county level)
  - USDA county level stocking
  - Dairy/meat emission factor
- Natural gas dist./use (county level)
  - County level facility/usage statistics (ARB)
- Wetlands (4 km)
  - NASA-CASA (Potter, 2006)
- Crop Agriculture (5 km)
  - County level DNDC (Salas et al., 2006)



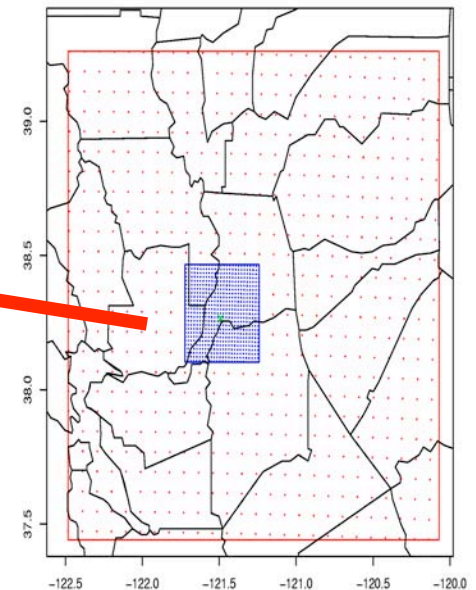
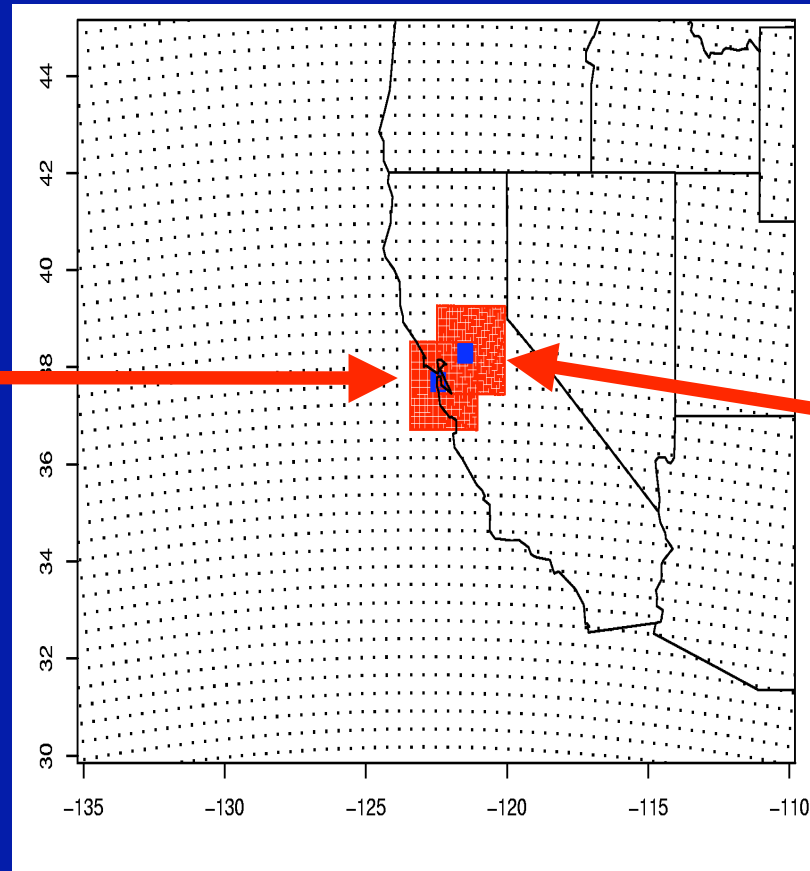
## Formal Inverse (2)

### WRF Meteorology for Tower Sites

- Outer grid covers Western US at 40 km resolution
- Middle grids cover Bay Area and Sac. Valley at 8 km resolution
- Inner grids cover Sutro and Walnut Grove sites at 1.6 km resolution



STR



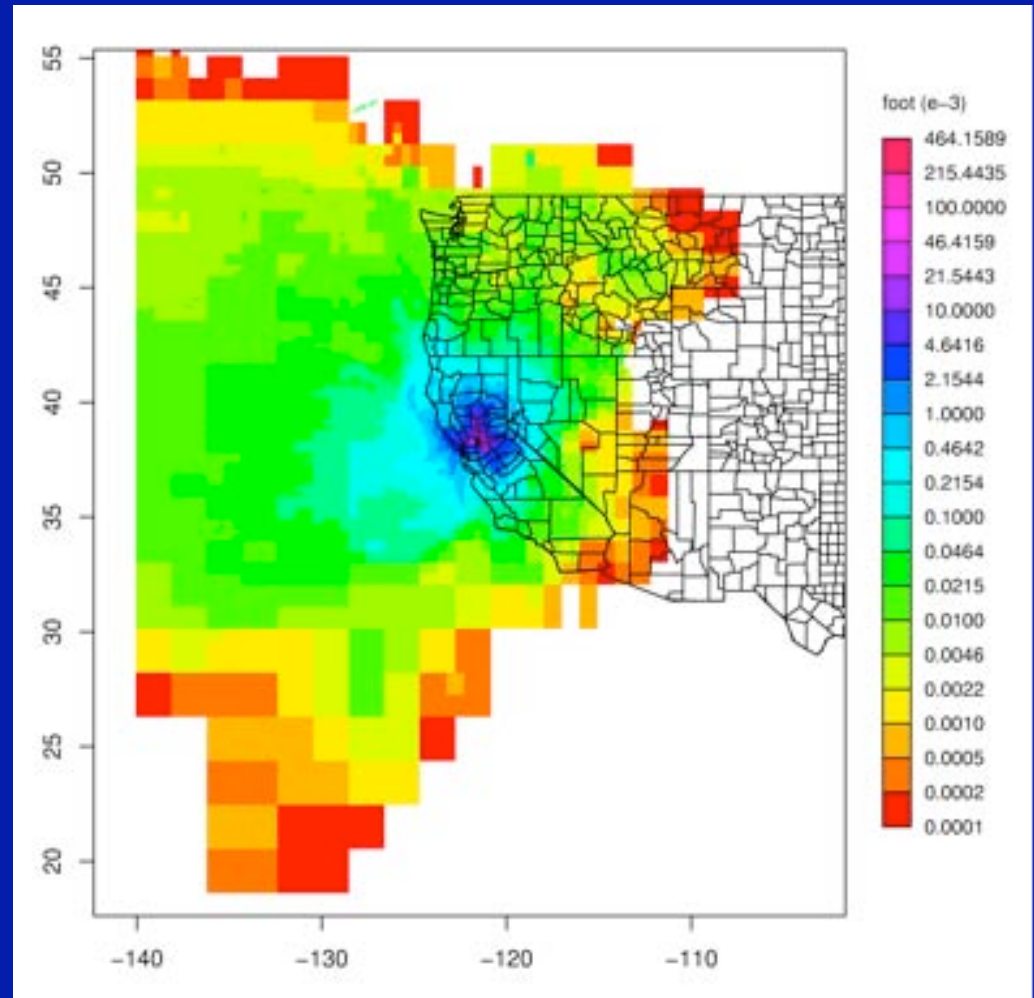
WGC

# Formal Inverse (3)

## WRF-STILT Footprints for WGC Tower

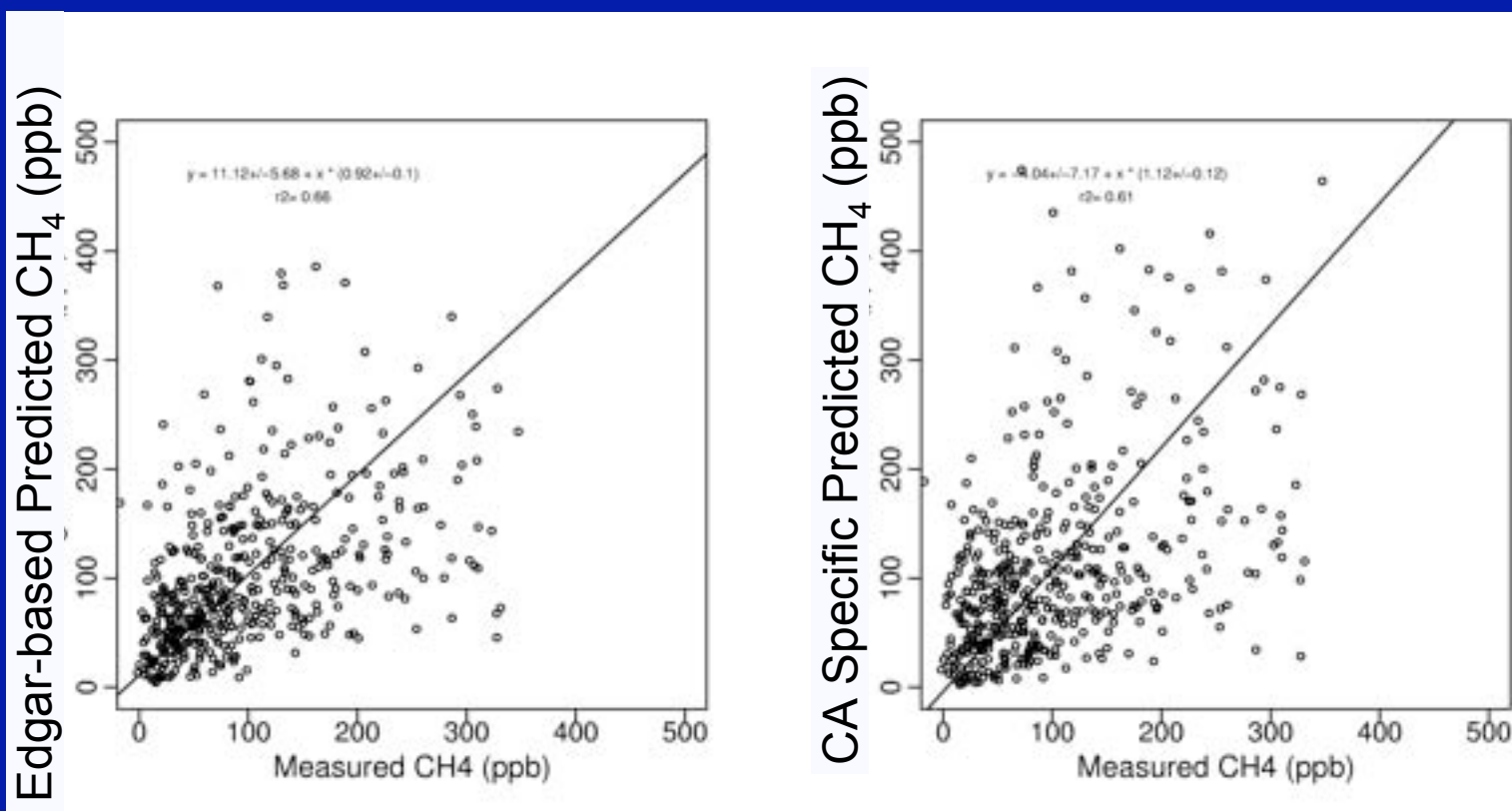
- Example of average footprint for Oct-Dec, 2007 (from hourly maps)
- Largest surface influences (purple) for Bay Area and Central Valley
- Use each hourly footprint maps to calculate predicted CH<sub>4</sub> signal

$$\text{CH}_{4\text{pred}} = F_{\text{CH}_4} * \text{foot}$$



# Measured and Predicted CH<sub>4</sub> : Regression Analysis

- Edgar and CA specific emissions estimates produce predicted vs. measured signals with similar slopes ( $0.92 \pm 0.1$  and  $1.12 \pm 0.12$  respectively)





# Formal Inverse (5): Posterior CH<sub>4</sub> Fluxes

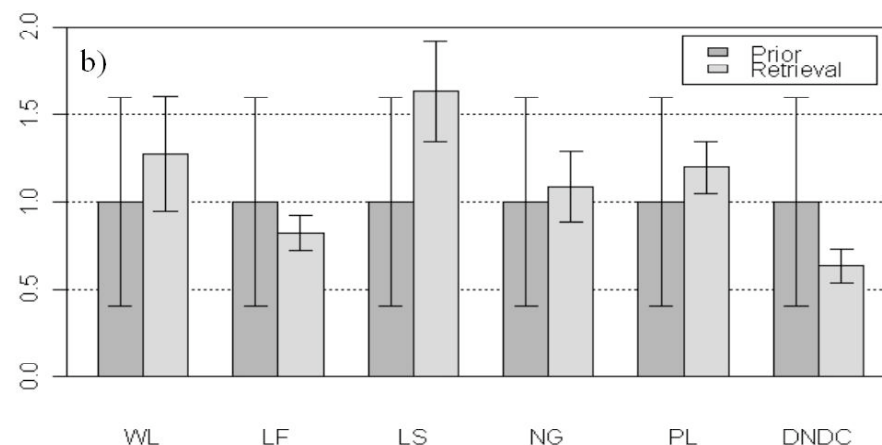
- Estimate scaling factors for each emission source in Bayesian approach
- *a priori* errors assigned at 30% for each source

## •Results:

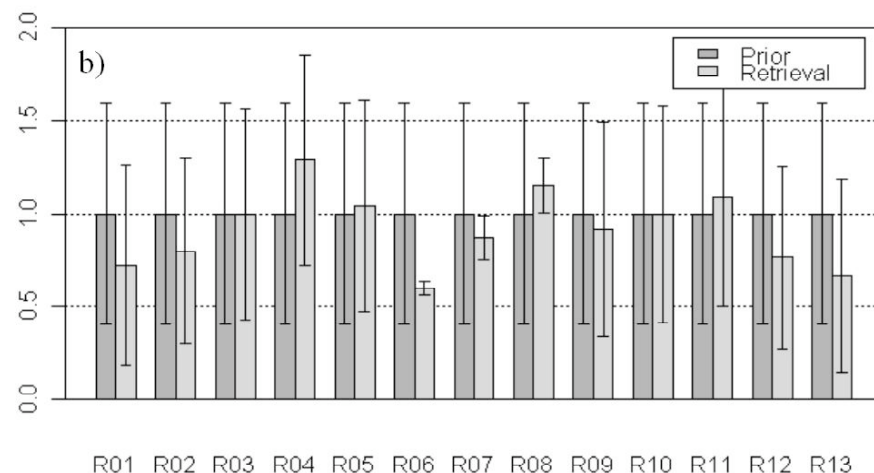
1) Source analysis retrievals estimate landfill and crop emissions smaller ( $0.8 \pm 0.05$ ,  $0.63 \pm 0.05$ ), and livestock emissions higher ( $1.6 \pm 0.15$ )

2) Region analysis retrievals demonstrate that only regions near tower are constrained by measurements (reducing uncertainties) while distant regions are not

## Source Analysis



## Region Analysis



# Summary

- Compliance with AB-32 requires verification of emissions reductions
- Atmospheric measurements provide independent and complementary test of inventories
- Non-CO<sub>2</sub> GHG particularly uncertain
- CALGEM measurements demonstrate that non-CO<sub>2</sub> GHG signals are readily measurable
- Gas-ratio emission estimates may constrain emissions but more work is needed
- Formal inverse approach combines data and model to refine *a priori* CH<sub>4</sub> emission estimates

## Further Work

- Quantitatively assess inverse model uncertainties
  - Include profiler data to assess meteorological model errors
  - Compare/combine gas-ratio and inverse methods
  - Combine data from WGC, STR, aircraft flights in inverse
- Measure other GHGs and tracers:
  - CO<sub>2</sub>: <sup>14</sup>CO<sub>2</sub> for combustion and fossil attribution
  - N<sub>2</sub>O: Formal inverse model (DNDC prior + automobile, other)
- Combine data across activities with other groups
  - CARB CO inventory as alternate tracer
  - ARCTAS measurements at WGC
  - Work toward multi-site data analysis system for CALNEX2010